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THE EFFECT OF PRESSURE UPON OPTICAL ABSORPTION.

BY FRANCES G. WICK.

INVESTIGATIONS ON LIGHT AND HEAT, MADE AND PUBLISHED WITH AID
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(Continued from page 3 of cover.)

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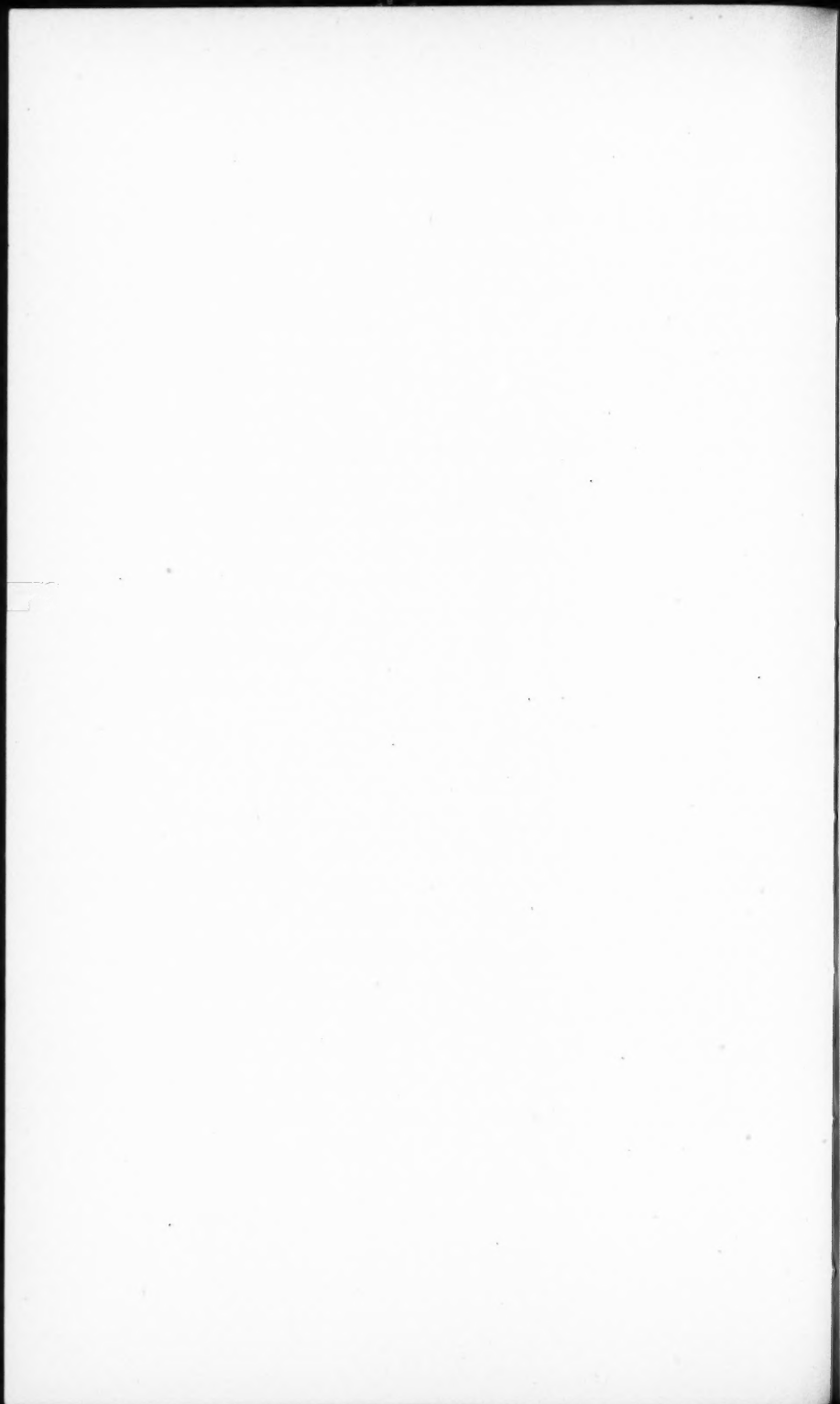
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THE EFFECT OF PRESSURE UPON OPTICAL ABSORPTION.

BY FRANCES G. WICK.

Presented by P. W. Bridgman.

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THE effect of pressure upon various optical properties of matter has been the subject of considerable research, a very good account of which is given in a paper by Wahl.¹ Experimental difficulties have greatly limited the results obtained in high pressure optical work since the pursuit of problems along this line involves the construction of apparatus having transparent windows which will stand high pressure without fracture and which are mounted in such a way as to prevent leaks. Little work has been done at pressures above 1000 atmospheres although Wahl occasionally succeeded in reaching a limit of 4000 atmospheres.

The work described in this paper was undertaken at the suggestion of P. W. Bridgman and it was done with pressure apparatus designed by him and manipulated under his supervision in the Jefferson Physical Laboratory, through the courtesy of Harvard University. Experiments were made upon the absorption of light in solutions and in solids up to pressures of 3500 atmospheres. The difficulties encountered were many and the results are principally qualitative but they appear to be of sufficient interest to warrant publication at this time since this is a field which has been left practically unexplored.

APPARATUS.

The part of the apparatus used for this work which has to do with the production, transmission, and measurement of pressure is similar to that commonly used by Bridgman² in different kinds of pressure experiments. The only parts of the outfit peculiar to this particular work were the observation chamber, in which the specimen under consideration was subjected to pressure, and the optical system used for the study of the absorption of light. The general arrangement of the apparatus is shown in Figure 1. The specimen, S, was mounted at the bottom of an observation chamber, O, made by drilling a hole $\frac{11}{16}$ of an inch in diameter and 7 inches deep along the axis of a steel

¹ Wahl, Phil. Trans. Royal Soc. London, Vol. 212A, p. 117.

² Bridgman, Proc. Am. Acad., 47, p. 321, 1911-12; 49, p. 627, 1913-14.

cylinder 8 inches in diameter and $8\frac{1}{2}$ inches high. Light from a small automatic carbon arc, A, made parallel by a lens, L, was transmitted through transverse openings in the cylinder in which were mounted glass windows at G, G. A Hilger spectrograph of the constant devia-

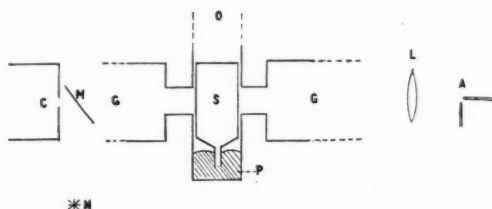


FIGURE 1.

tion type was so placed that the collimator, C, was in line with the light transmitted through the specimen, S. A cadmium spark, N, was used as a comparison source, and a movable mirror, M, was used to reflect this light into the collimator.

For the study of liquids, the specimen, S, was contained in an inverted cylindrical glass bottle, as shown in Figure 1, with a narrow neck which dipped into mercury, P, to prevent the mixing of the oil through which the pressure was transmitted, with the solution under observation. When the apparatus was used for the study of solids, the specimen was placed in a brass holder mounted in position S.

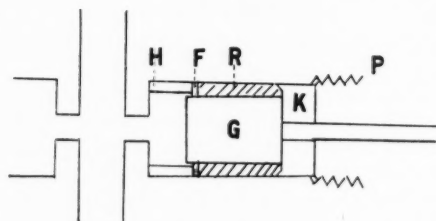


FIGURE 2.

The details of mounting the glass windows are shown in Figure 2. The cylindrical windows were cut from a piece of plate glass $1\frac{1}{4}$ inches thick and were so mounted that a rubber washer, R, a short piece of

pure rubber tubing, filled the space between the glass and the steel. The washer was wrapped with fine thread after it was put on the windows in order to make it possible to insert the window and the washer into the opening. The thread breaks upon tightening the packing when the plug is screwed in at P. A thin fibre washer, F, placed at the end of the steel bearing, H, served as a guide for the window. A piece of thin paper was placed between the end of the window and the steel bearing, K, which was held in place by the plug screwed in at P. A hole $\frac{3}{16}$ of an inch in diameter through the center of the bearing and the plug allowed for the transmission of light.

Pressure was supplied by a hand pump of 1000 kg per sq. cm. capacity connected to an intensifier having a piston ratio of 4 to 1. The intensifier served to separate the pump liquid from the clear oil in the optical parts. A manganin pressure gauge was inserted between the intensifier and the plug at the top of O, Figure 1, through which connection was made with the observation chamber.

PROCEDURE.

The observation chamber, O, Figure 1, was filled with neutral white oil, the medium used for the transmission of pressure, and air bubbles were removed by means of a vacuum pump. A steel container holding the mounted specimen was lowered into position S, and the plug through which connection was made to the intensifier was screwed into the top of O. The source of light, A, the lens, L, and the collimator of the spectroscope, C, were then placed accurately in line with the windows, G G and the specimen, S.

The spectrum of the light transmitted through the specimen was photographed, first, at normal pressure, then, after the pressure was raised. By use of a divided slit, the two exposures were made adjacent to each other and the comparison spectrum was photographed on the edge of each without any change in the adjustment of the apparatus. For most of the work Wratten and Wainwright panchromatic plates were used but for the study of absorption bands of greater wave-length than 7000 Ångstrom units, Seeds 26 plates dyed with Eastman red-sensitive dye were prepared. Simultaneously with the taking of the picture of the absorption spectrum, the corresponding pressure was determined by measuring the change in resistance of the manganin gauge.

DIFFICULTIES.

Glass is a very unreliable substance when subjected to high pressure and the breaking of the windows of the apparatus caused considerable trouble. It was difficult to mount the windows in such a way that they should not become cramped against some part of the steel when the pressure was raised. This was especially likely to happen if the ends were not accurately perpendicular to the axis, which was doubtless the case with some of the windows used since they were made by grinding cylindrical pieces from thick plate glass such as is used in portholes of ocean liners. The curved surfaces were finished off in the lathe and made true but no attempt was made to grind and polish the faces of the windows. The final mounting, shown in Figure 2, seemed reasonably safe. The fibre washer, F, slightly wider than the shoulder, H, was inserted to prevent the crowding of the glass against this shoulder in case the outer face of the window was not exactly perpendicular to the axis.

A second difficulty arose from the fact that, at high pressures, the rubber of the washers dissolved in the neutral white oil used in the observation chamber. This caused a diminution in the intensity of the transmitted light which took place gradually after the application of pressure and caused considerable trouble at pressures above 2000 atmospheres. When the apparatus was allowed to stand at pressures of this order, the absorption of light continued to increase, a difficulty which proved very serious since the work was done photographically and red-sensitive plates which required long exposures were used. Upon relieving the high pressure after it had been maintained for some time, the light transmitted through the specimen came back to almost its original brightness at a pressure of approximately 2000 atmospheres. After the pressure had been run up and down several times, the intensity of the light transmitted at normal pressures was somewhat diminished and, upon removal of the specimen from the observation chamber, the oil next to the windows was found to be cloudy, due to the gradual disintegration of the rubber washers which had to be replaced from time to time to prevent leaks. Different varieties of oil were tried and a heavy variety called "Nujol" was found to cause the least trouble. By changing the oil in the observation chamber frequently the difficulties due to lack of transparency in "Nujol" were largely eliminated.

A comparison of the relative intensities of light transmitted by a given specimen at different pressures is a matter of interest but no

such comparison can be made with the apparatus so constructed as to bring rubber washers in contact with oil at high pressures. If this source of trouble could be removed, it would then be desirable to substitute for the arc a more constant source of light. Nitrogen filled tungsten lamps, the "pointolite" and a tungsten arc kindly furnished by the General Electric Company were tried for this work but were found unsatisfactory because of the increase in the time of exposure required with a less intense source of light. This made the difficulty due to the gradual dissolving of the washers more marked.

SELECTION OF MATERIAL.

The work was begun upon substances having well-marked absorption bands, a number of which were known to show some change in the bands upon variation in temperature or concentration, since it seemed desirable to make a comparison of any possible pressure effect with variation in absorption already known to be due to other agencies. After a preliminary study of various absorbing materials, the following were selected for study:

Aqueous solutions of salts of the rare earths neodymium, praseodymium, erbium and "didymium."

Aqueous solutions of the uranyl salts.

Aqueous solutions of cobalt chloride.

A synthetic ruby.

Samples of colored glass.

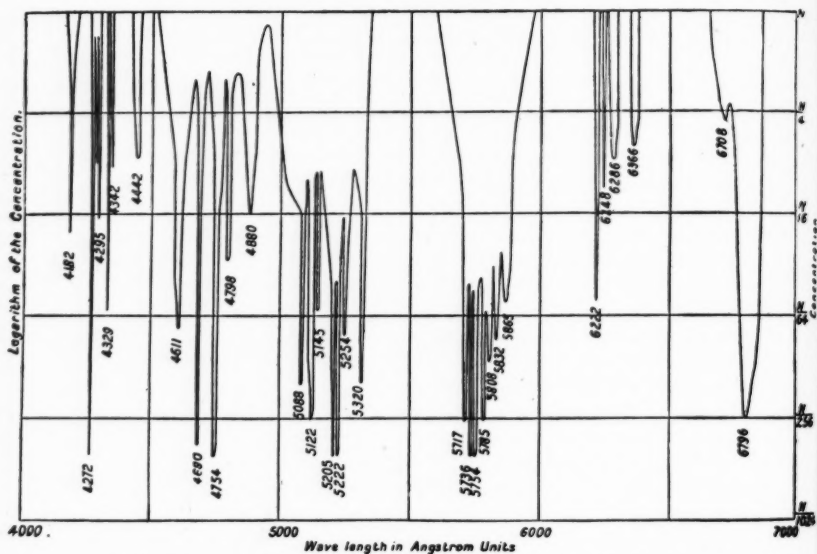
NEODYMIUM SOLUTIONS.

The absorption spectra of aqueous solutions of neodymium salts are known to be rich in bands of unusual sharpness which are much alike for dilute solutions of different salts. Neodymium ammonium nitrate, obtained through the kindness of the Welsbach Company, was the salt used for most of this work but a number of observations were also made upon the nitrate, chloride, and acetate formed from pure neodymium oxalate obtained from Professor James of New Hampshire University.

As is well known, the bands are not all visible under the same conditions but different ones may be brought out by varying the thickness and concentration of the absorbing layer. In these experiments the thickness of the absorbing specimen was limited by the size of the

observation chamber to about 1.4 cm. and it was possible to vary only the concentration of the solution in order to bring out different bands. The exact concentration of solution used was not known except in the case of neodymium ammonium nitrate solutions which varied from .0698 to .693 normal.³

The position and width of the absorption bands in dilute solutions



Absorption spectrum of aqueous neodymium chloride (Rech; thickness of absorbing layer = 20 cms.).

FIGURE 3.

of neodymium salts for different concentrations⁴ are shown in Figure 3 taken from the work of Rech⁴ and copied directly from Little's⁵ book. Along the horizontal axis, the width of the various absorption bands in Angstrom units is indicated for different concentrations which are

³ The term "normal solution" is used to indicate one that contains the same number of grams of solute per liter of solvent as the number which represents the molecular weight of the salt dissolved.

⁴ Rech, *Zeits. Wiss. Photochem.*, 1905, 3, 411.

⁵ Little, *Text-book of Inorganic Chemistry*, Vol. IV, p. 290.

shown on the vertical axis. The figure shows nothing with regard to relative intensities of bands but it gives a good idea of the absorption bands present in different concentrations. For most of the high pressure work, a .2 normal solution was found to be most satisfactory which, with the thickness of about 1.4 cm. of cell used in the apparatus, gave an absorption spectrum comparable with that of an N/64 solution 20 cm. thick as shown in Figure 3.

An increase of pressure was found to produce changes in the appearance of the absorption spectra of neodymium solutions which were observed both visually and photographically but which, on account of the low dispersion of the spectrograph used, are not of sufficient magnitude to reproduce satisfactorily. In general, the following changes in the absorption spectra accompany an increase of pressure:—

1.—Some bands show a marked change with pressure increase while others show little or no effect. The bands most affected are the group between 5717 and 5865, the doublet 5205 and 5222, and the sharp blue band 4272. (The first group of these bands will be referred to hereafter as band 5800, and the doublet will be referred to as band 5200.)

2.—The effect of increase in pressure is to narrow and intensify the bands and to cause the component bands of a group to become more distinctly resolved. The narrowing of the bands is usually unsymmetrical, most of the reduction in width taking place on the red side.

3.—Some bands which are weak and diffuse at normal pressure are brought out at high pressures.

4.—An increase in pressure causes a slight shift in the position of certain bands in the red end of the spectrum toward the violet and a shift of the sharp blue band, 4272, toward the red.

Neodymium Ammonium Nitrate.

A very sharp absorption band at 7324,⁶ not shown in Figure 3, which came out only on plates dyed to make them red-sensitive, was shifted toward the shorter wave-lengths upon application of 3500 atmospheres pressure. The width of this band is about 20⁷ Ångströms

⁶ The wave-length of this band is taken from Little's Text-book of Inorganic Chemistry, p. 288.

⁷ The values given for the width, narrowing, and shift of absorption bands are only approximate since the poor definition of some of the bands and the

and the shift amounts to from 3 to 6 Ångströms. This band is sharply defined at normal pressure and its appearance is not perceptibly changed by pressure.

The most conspicuous effect of pressure is that shown upon the prominent group of bands at 5800. In the photographs taken at normal pressure, this group appears as a single band showing very little resolution, which terminates sharply on the violet side but shades off gradually toward the red. The effect of pressure is to narrow and intensify the components of the group so that they appear more sharply defined and distinctly separated in the central and short wave-length end of the band, and to narrow the whole band by cutting off or weakening the long wave-length end. In some concentrations, the component of longest wave-length is practically suppressed by pressure. There is also a slight shift of the violet side of this group toward the shorter wave-lengths. In a .2 normal solution a pressure of 1700 atmospheres causes a shift of approximately 5 Ångströms on the violet side of this band and a narrowing of about 20 Ångströms on the red side.

The double band at wave-length 5200 having a width of about 25 Ångströms in a .2 normal solution has its components decidedly sharpened and intensified by the application of a pressure of 1700 atmospheres. There also appears to be a very slight shift of the violet side of this band toward the shorter wave-lengths, amounting to 1 or 2 Ångströms, together with a narrowing on the red side of 3 or 4 Ångströms.

The fine blue band at 4272 was made narrower and sharper by pressure and it was also intensified and shifted toward the red, the opposite direction from the shift observed in the case of the red bands. Jones and Strong⁸ have described this band as varying in appearance in different solutions, sometimes appearing double and sometimes single. In the more concentrated solutions observed in this work, this band appears double with the dimmer component on the side toward the longer wave-lengths. This component is weakened or caused to disappear by an increase in pressure while the stronger component is sharpened and intensified. The total width of the band in a solution .287 normal at ordinary pressure is about 15 Ångströms. The effect of a pressure of 1500 atmospheres is to narrow the red side

uncertainties arising from differences in exposure of the plates make exact measurements impossible.

⁸ Jones and Strong, Carnegie Publication 130, p. 84.

about 8 Ångströms, to shift the violet edge about 2 units toward the longer wave-lengths, and to reduce the width of the whole band to about 5 units.

Bands 5088 and 5122 are somewhat narrowed by pressure and the separation between them is made more distinct. 4690, 4611 and 4329, are slightly narrowed and intensified by pressure but the effect is very small. The group of red bands, 6730,⁹ 6790, and 6890, appearing only in the more concentrated solutions, is made more distinct by pressure.

In the neodymium ammonium nitrate solutions, band 4754, shown in Figure 3, did not appear. Two broad, hazy bands not shown in this figure, at wave-lengths 4410 to 4465 and at 4813, were observed which were evidently due to an impurity of praseodymium. No decided effect upon either of these bands could be noticed when the pressure was raised.

Neodymium Nitrate.

Solutions of neodymium nitrate, prepared from pure neodymium oxalate obtained from James, show a pressure effect which is similar to that observed in the ammonium nitrate. An excess of free acid seems to increase the effect. The band at 5800 which, at normal pressure shows itself to be made up of several poorly defined components, is resolved and intensified by a pressure of 2500 atmospheres. It is made narrower on the red side and the components of the group which are of longest wave-length disappear at this high pressure. The band at 5200 is sharpened and intensified and the band at 4272 which is not so sharp as in the ammonium nitrate, is made narrower and slightly shifted toward the red.

Neodymium Chloride.

The effect of pressure upon neodymium chloride is similar to that observed in the nitrate but much smaller. The components of the groups at 5800 and 5200 were more distinct at normal pressures than in the nitrate but the effect of pressures from 1500 to 1800 atmospheres was exceedingly small. Concentrations were used which were greater than those of the other salts and bands appeared between 6222 and 6366 which did not show in the nitrate solutions. These were slightly intensified by pressure and the red bands, 6730, 6790, and 6890 were also intensified and slightly shifted toward the violet.

⁹ Wave-lengths taken from Little,—Text-book of Inorganic Chemistry, Vol. IV, p. 288.

Neodymium Acetate.

The absorption of neodymium acetate¹⁰ differs from that of the other salts in that the bands are shifted toward the longer wavelengths and are much more diffuse. Single, unresolved bands appear instead of the groups of narrower bands seen in the other salts at the corresponding concentrations. A pressure of 1440 atmospheres produces a slight intensification of the band at about 5800 and separates it more distinctly into its two components.

"Didymium" Nitrate.

Didymium is a mixture of praseodymium and neodymium and the spectrum of the nitrate is similar to that of the neodymium ammonium nitrate and shows the same pressure effects. In the concentrations used, aqueous solutions of didymium nitrate show very distinctly the two components of band 4272 at normal pressure. At a pressure of 1700 atmospheres, the dimmer component practically disappears and the stronger one becomes sharper and more intense.

EFFECTS OF CHANGES IN TEMPERATURE AND CONCENTRATION UPON NEODYMIUM ABSORPTION SPECTRA.

Effects very similar to those due to increase of pressure have been observed as a result of the lowering of the temperature of neodymium solutions.¹¹ Jones and his colleagues, in an extensive series of investigations of aqueous solutions between 0° and 190°, found that all absorption bands have a tendency to become more diffuse at high temperatures but that no marked change in the appearance of the bands takes place except in the cases of 4272 and 5800, both of which remain fixed on the violet edge and widen on the red edge diffusely with rise in temperature. These two bands are the ones most changed by an increase in pressure and it is observed that the effect of raising the pressure is to produce an unsymmetrical narrowing similar to that produced by a reduction of temperature. It is known from the work of Becquerel,¹² Du Bois and Elias¹³ and others, that the absorption

¹⁰ Jones and Strong, Carnegie Publication, 130, p. 79.

¹¹ Jones and Strong, Carnegie Publication 130, pp. 72, 77, 83. Jones and Guy, Carnegie Publication 190, p. 9.

¹² Becquerel, Phil. Mag., Vol. 16, p. 153, 1908.

¹³ Du Bois and Elias, Ann. der Phys., Vol. 27, p. 233.

bands of solutions and of crystals of the rare earth salts become finer and increase in intensity with lowering of temperature and are remarkably narrow at the temperature of liquid air. Becquerel states that the width of the absorption bands in some substances varies proportionally with the square root of the absolute temperature and that the total amount of energy absorbed at low temperatures is greater than the total amount absorbed at high temperatures.

Marked changes are also produced in the absorption spectra of neodymium solutions by changes in concentration as may be observed from Figure 3. Bands 5800, 5200, and 4272, the ones most affected by variations in pressure or temperature, are also most influenced by changes in concentration. These bands are resolved and narrowed unsymmetrically by dilution much as they are by either increasing the pressure or lowering the temperature. The resemblance between the effects of pressure and dilution upon band 4272 is especially marked as may be observed by comparing the pressure effect described in this paper with the effect produced by dilution as described by Jones and Anderson.¹⁴

The changes produced in the neodymium absorption spectra by increasing the pressure, lowering the temperatures or by dilution are similar to those which have been observed by Nichols and Howes¹⁵ in the uranyl salts upon lowering the temperature to that of liquid air. The absorption bands of these salts occur in groups which are poorly resolved at ordinary temperatures. The component bands of the groups are sharpened and intensified by reduction in temperature and the envelope of the individual groups, as well as the envelope of the groups taken as a whole, is pinched off more on the red side than on the violet side. Some bands which appear on the red side of the group at 20° are weakened or caused to disappear entirely by a reduction of temperature to -180°. In general, the effect of cooling is that the absorption spectrum, considered as a unit, suffers a narrowing on cooling which is more marked toward the red than toward the violet end.

PRASEODYMIUM SALTS.

The absorption bands of praseodymium salts are wide and poorly defined and the effect of pressure upon the solutions observed in this work, the sulphate and the nitrate, was found to be very small. A

¹⁴ Jones and Anderson, Carnegie Publication 110, p. 88.

¹⁵ Nichols and Howes, Carnegie Publication 298, Ch. V, pp. 61, 79.

solution of praseodymium sulphate, .083 normal concentration, made from material furnished by the Welsbach Company, showed little change when subjected to a pressure of 1700 atmospheres. A nitrate solution made from pure praseodymium oxalate furnished by James, showed a narrowing and intensifying of the components of the broad band with crests at 5882 and 5964. Bands at 4813 and 4688 appeared to have their red sides shifted slightly toward the red but these bands are not sharp and the effect is doubtful.

From observations made by other observers, it is known that the absorption bands of praseodymium solutions change very little with variations in temperature and concentration in comparison with the changes which occur in solutions of the neodymium salts.

ERBIUM NITRATE WITH YTTRIUM.

Erbium nitrate with traces of yttrium in aqueous solution made from material furnished by James, shows an absorption spectrum in which some of the bands are very narrow and sharp. The effect of a pressure of 1500 atmospheres was found to be so small that it appeared uncertain as to whether or not any change took place. Bands 6535 and 6490 and the very narrow crest at 5231 appeared to be narrowed and intensified by pressure.

URANYL SALTS.

Solutions of the uranyl salts were suggested by E. L. Nichols as substances upon which to try the effect of pressure. The absorption bands in aqueous solutions of uranyl potassium sulphate and uranyl ammonium chloride appeared to be made somewhat more distinct by a pressure of 1500 atmospheres but the effect was not pronounced.

COBALT CHLORIDE.

Aqueous solutions of cobalt chloride are well known to be sensitive to variation in temperature, changing from a purplish-red color at room temperature to a decided blue at higher temperatures in the more concentrated solutions. As a result of repeated observations of the absorption spectra of solutions varying from .2 to 1.6 normal, at pressures up to 1500 atmospheres, the conclusion may be drawn that the effect of increasing the pressure is similar to that of lowering the temperature. There is a broad absorption band in the middle part of the visible spectrum with transmission bands at both ends,

the width of this absorption band varying with the concentration and thickness of the solution used. Some of the photographs of the spectra of these solutions showed that, upon increase of pressure, the transmission in the red end of the spectrum was increased and that in the blue end was decreased causing the color of the transmitted light to become more red at higher pressures as it does at lower temperatures, the greatest change taking place in concentrated solutions. The wide, diffuse absorption band having its center at about 5200 was observed to change its limits with increase of pressure but no quantitative measurements could be made on account of difficulties already mentioned in connection with the apparatus.

GLASS.

Samples of glass made at the Corning Glass Works, some of which were known to change color with variation in temperature, were obtained through the kindness of Dr. H. P. Gage. The effect of pressure upon these specimens was such as to produce a change in color in some but not in others.

No observable effect was produced upon the absorption spectra of canary glass, a blue-green variety marked 4102¹⁶ or upon "Didymium" glass by a pressure of 1400 atmospheres. In the last mentioned, the didymium bands were similar to those observed in concentrated solutions of the salts of this substance and such solutions did not show the marked change with pressure which was observed in the more dilute solutions.

Orange glass, G 34, was observed, at a pressure of 3700 atmospheres, to become more yellowish in color due to a shifting of the transmission band which is in the red end of the spectrum, toward the shorter wave-lengths. Orange glass, G 36, has a similar color change, becoming more yellowish under 1300 atmospheres pressure. The single transmission band is cut off more on the red side than on the violet side by an increase of pressure. A red glass, G 20, has a much stronger transmission band at high pressures than at low and the band is extended toward the shorter wave-lengths. That the intensity of the transmitted light is increased at high pressure can easily be observed both visually and photographically.

A comparison of the changes in absorption due to pressure with those due to variation in temperature shows that an increase of pres-

¹⁶ The numbers given are those sent by Dr. Gage with the different specimens of glass.

sure upon at least three specimens of the glass produces an effect which is similar to that produced by lowering of temperature. Gibbs,¹⁷ in his work upon colored glass at high temperatures, found that the effect of heating is, in most cases, to increase absorption and to shift the absorption bands toward the longer wave-lengths. Gibson,¹⁸ in a study of colored glass at low temperatures, found that the transmission becomes greater at low temperatures and that absorption bands are generally shifted toward the violet. A specimen of orange glass was found by him to become more yellow at -180° and a brilliant red at 430° . A similar increase of transmission and shift of absorption bands toward the red with increase of pressure has been described in the case of glasses of red and orange color, G 20, G 34, and G 36.

SYNTHETIC RUBY.

A synthetic ruby 2.8 mm. thick kindly furnished by E. L. Nichols, showed a small change in absorption at pressures up to 1600 atmospheres. Absorption bands with centers at 6688, 6593, 4768, and 4687 were slightly intensified by pressure and the characteristic close doublet which, according to Gibson,¹⁹ has its components at 6943 and 6928 at room temperature and looks practically like a single band at room temperature and normal pressure, is slightly sharpened by pressure so that the components are more distinct and the band appears to be shifted by a very small amount toward the violet.

DuBois and Elias,²⁰ Mendenhall and Wood,²¹ and Gibson²² have investigated the effect of decrease of temperature upon absorption in the ruby and they all found the narrow red doublet to be sharpened and more distinctly resolved. It is also shifted toward the violet about 9 Ångströms with lowering of the temperature to -180 degrees. Numerous absorption bands of wave-length between 6950 and 7100 were observed by DuBois and Elias and by Mendenhall and Wood at liquid air temperatures. Gibson did not observe these bands but his results show two bands at 5905 and 5965 breaking off from the broad absorption band at these low temperatures and also a change in the position of the maximum of this absorption band.

¹⁷ Gibbs, *Phys. Rev.*, Vol. 31, p. 463, 1910.

¹⁸ Gibson, *Phys. Rev.*, Vol. 7, p. 194, 1916.

¹⁹ Gibson, *Phys. Rev.*, Vol. 8, p. 38, 1916.

²⁰ Du Bois and Elias, *Ann der Phys.*, Vol. 27, p. 233; Vol. 35, p. 617.

²¹ Mendenhall and Wood, *Phil. Mag.*, Vol. 30, p. 316.

²² Gibson, *Phys. Rev.*, Vol. 8, p. 38.

The effect of pressure upon the ruby is similar to that of a lowering of temperature in that the characteristic red doublet is sharpened and shifted toward the violet by both agencies. An increase in pressure did not, however, bring out the bands which are referred to by the investigators mentioned as coming out at low temperatures.

SUMMARY.

A comparison of the pressure effects with those due to other agencies shows that, in general, the changes which take place in the absorption spectra upon increase of pressure are similar to those which take place upon lowering the temperature or decreasing the concentration. The similarity of these three effects, especially in the case of neodymium solutions, is very marked in that the same absorption bands are affected in the same way, becoming narrower and sharper unsymmetrically. There are, however, some differences in the effects due to these different sources. There is a slight shift in the position of the neodymium bands upon increase in pressure which does not take place upon lowering of temperature or decrease of concentration. This shift is, as has been mentioned, toward the red in most cases but toward the violet in the case of band 4272. The only neodymium solutions which show appreciable shift with rise in temperature are those ²³ to which some dehydrating agent such as calcium chloride has been added. It is also observed that bands barely visible under normal conditions are brought out more strongly by either increase of pressure or lowering of temperature but this effect is not produced by dilution. In order to bring more bands into prominence by change in concentration, solutions of neodymium salts must be made more concentrated rather than less as may be observed from Figure 3.

It is not possible, from the observations made in this work, to make any exact quantitative comparison of the effects upon the absorption spectra due to different agencies but a study of the photographs of the absorption spectra of neodymium ammonium nitrate taken at different pressures, temperatures, and concentrations makes possible a rough estimate of relations. The lowering to the temperature of liquid air of a thin layer of concentrated solution of neodymium nitrate giving an absorption spectrum at room temperature similar to that observed in some of the solutions used for pressure work, produced a much greater effect in sharpening and intensifying the bands

²³ Jones and Strong, *Am. Chem. Jour.*, Vol. 43, p. 130.

than that which was observed in the highest pressures used in these experiments. The effect of a pressure of 3500 atmospheres was about equal to the effect due to the lowering of temperature which took place when the cooled specimen was supported in a Dewar flask above liquid air and attached to a metal strip, the lower end of which dipped into the liquid air. The temperature of this specimen was not measured but a rough estimate indicates that it was at least 60 below zero centigrade. A comparison of the pressure and concentration effects shows that an increase of 1700 atmospheres pressure upon a .2 normal solution of a neodymium nitrate is approximately equivalent to a reduction of the concentration of this solution to one half its value, that is, to making the concentration of the solution .1 normal.

The changes observed in the absorption spectra upon increase of pressure cannot be explained by any actual temperature or concentration change which might take place as a result of pressure since any direct effect due to either of these sources is known to be usually in the opposite direction. Upon application of pressure, the specimen becomes warmer but the heating effect amounts to only a few degrees with the highest pressures used and this slight rise in temperature rapidly disappears in the heavy steel cylinder. If correction were to be made for it, the corrected value of the pressure effect would be larger than the observed effect. Upon application of the highest pressures used, the actual volume of the aqueous solutions was decreased about 10 per cent. If this decrease of volume under pressure is equivalent to an increase in concentration, the effect of it should be to broaden rather than narrow the bands, and correction for it should make the actual pressure effect larger than the observed effect.

The fact that such agencies as variations in pressure, temperature, and concentration affect some of the absorption bands of solutions but not others and the fact that the bands affected undergo changes which are not the same for different bands, seem to indicate that there must be more than one simple type of mechanism involved in the production of these absorption bands.

From a comparison of the absorption bands of neodymium crystals with those of the same salts in solution, it is observed that the bands in the crystals are sharper than those in the solutions under normal conditions. Since absorption bands in solutions are made sharper by pressure, it seems possible that solutions under pressure may have something approaching structure tending to make the bands more as they are in the solid state. However, until more is known about the mechanism of the absorption of light, an explanation of the

change in absorption due to increase in pressure and the relation of this effect to the effects produced by lowering of temperature and decrease in concentration, confront the experimenter as difficult problems to be solved eventually by the theoretical physicist.

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